THE FORMATION OF SULPHUR TRIOXIDE AND
CALCIUM SULPHATE IN THE SULPHITE PROCESS.

ABSTRACTS FROM THE LITERATURE

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Introduction by H. O. Teeple
As an introduction to a review of the bibliography: "The Formation of Sulphur Trioxide and Calcium Sulphate in the Sulphite Process .... Abstracts from the Literature," after a very brief statement of the types of acid pulping processes and certain operations therein, the types and mechanisms of corrosion to which stainless steels are susceptible are outlined. Following this approach, certain of the abstracts are cited specifically and discussed as being directly concerned with SO$_3$ formation and consequent possible effect on the performance of stainless steels.
The sulphite process, first discovered in 1866, is the oldest chemical process for producing a suitable paper pulp from a fibrous raw material. There are four bases commercially employed at present:

a. Calcium base
b. Magnesium base
c. Ammonium base
d. Sodium base

and the last three are generally described as soluble base processes. However, all four employ certain operations which are more or less identical. These are burning sulphur to make sulphur dioxide, cooling the burner gas, transporting the cooled gas to the absorption towers, absorbing the SO₂ gas in the base solution, transporting the cooking liquor to a storage tank or to the digester, heating the cooking liquor, handling digester relief gases and dispensing the waste liquor.

Corrosion problems can occur in many of these operations and can vary, depending upon several factors such as the type of base used and the presence of either SO₂ or sulphuric acid. Many years ago, acid-resisting bronzes were used but frequent replacement was required because of its inadequate resistance to corrosion by the acid process liquors.

About 1928, austenitic stainless steels began to replace the bronzes for handling the acid process liquors, and many of the corrosion problems were thus alleviated. Currently, Type 316 Stainless Steel, or its equivalent, is more or less a standard material of construction for many acid pulping applications. It is important to note that corrosion problems
are still encountered. A number of these problems can be traced to the presence of \( \text{SO}_3 \) with consequent formation of sulphuric acid and gypsum in the case of the calcium base (insoluble sulphates are not formed in the case of soluble bases). It was felt desirable to review the literature to ascertain those studies which might be helpful in solving some of the corrosion problems.

Before an analysis is made of the literature references, it is believed desirable to describe some of the types and mechanisms of corrosive attack to which stainless steels are susceptible.

Stainless steels owe their resistance to corrosion to the formation and maintenance of an invisible, but yet real, oxide or oxygen film on the surface. Any environment which tends to destroy this film or prevent it from forming will cause corrosion of the alloy. Because the protective film involves oxygen, stainless steels are more resistant to corrosion by oxidizing environments than by reducing environments. Since sulphurous acid solutions are oxidizing in nature with respect to a metal or an alloy, the stainless steels, particularly the chromium-nickel-molybdenum variety, i.e. Type 316, will resist attack by these solutions quite well. On the other hand, stainless steels are suitably resistant to corrosion by sulphuric acid solutions only under limited conditions of acid concentration and temperature. Hot, concentrated sulphuric acid solutions dissolve the protective film on the surface of the alloy and as a consequence, rapid attack of the alloy will occur. Therefore, it is reasonable to conclude that one should avoid or, at least, minimize the occurrence of sulphuric acid.
Stainless steels are susceptible to another type of corrosion which, unfortunately, can occur frequently in acid pulping processes. This type of corrosion is commonly called crevice corrosion or oxygen-concentration cell attack. As the name implies, corrosion takes place when crevices occur wherein the alloy is either one or both components of the crevice. This attack will occur under deposits, such as gypsum scale and/or pulp fiber accumulations. The mechanism is essentially galvanic in nature. Two separate areas will show a potential difference and a corrosion current will flow. In a crevice, that portion of stainless steel under the deposit, or within the crevice, will be anodic (active) because the oxidizing power of the solution is low. On the other hand, that portion of the stainless steel outside the crevice, or the deposit, will be cathodic (passive) because the oxidizing power of the solution is high. Thus, the anodic area will be attacked and this is readily identified as the corrosion will always take place under the deposit.

While it has been indicated that this type of corrosion can occur in calcium-base pulping because of gypsum scale formation, it does not occur in soluble-base pulping for this reason because insoluble sulphates are not formed. It is important to note, however, that if crevices are formed because of other reasons than a chemical precipitate, this type of corrosion can occur even in the soluble-base processes. Therefore, it is reasonable to conclude that one should avoid or, at least, minimize the occurrence of crevices.

In passing, it is probably worthy of note that certain contaminants which may be present can cause serious corrosion of stainless steels. A specific contaminant is the chloride ion, and its presence is usually associated with mills located on tide water or utilizing tide-water floated...
wood. Serious pitting or localized corrosion frequently will occur, and the
austenitic stainless steels are particularly susceptible to stress corrosion-
cracking in hot acid environments contaminated with chlorides and especially
where there is an opportunity for the chlorides to become concentrated by
evaporation.

In addition to weight loss corrosion, crevice corrosion, and upon
occasion, stress corrosion cracking, the stainless steels are susceptible to
intergranular corrosion in acid-base pulping environments if the alloy is in
a sensitized condition. Sensitization can occur in some alloy compositions
during welding or stress relief heat treatments. Practical procedures avail-
able to avoid this type of corrosion include the use of a 0.03% maximum
carbon analysis or a stabilized alloy, as well as the employment of a solu-
tion heat treatment applied after fabrication by welding.

A review of the annotated bibliography reveals a number of helpful
references which may be grouped into certain categories for convenience in
discussion. An outline of these categories is:

**SO₃ in Burner Gas**

- Operation of Sulphur Burners
- Effect of Catalysts
- Effect of Cooling Rates
- Use of Electrostatic Precipitators

**SO₃ in Acid Making**

- Effects of Operational Procedures
- Effect of Catalysts

**SO₃ in Digesters**
Effect of Air in the Chips

Effect of Catalysts

Effect of Operational Procedures

Sulphate Formation

Corrosion

SO₂ in the Burner Gas

There are 21 references (1, 4, 11, 12, 16, 19, 26, 37, 42, 47, 48, 51, 52, 58, 61, 62, 74, 76, 85, and 88) having to do with the fact that the operation of sulphur burners has an effect on SO₂ formation. Mention is made of the desirability of controlling the purity of the sulphur (76), amount of excess air (16, 37, 51, 73, and 88) and moisture in the sulphur (58) to minimize SO₂ formation. Combustion temperatures appear to be important with uniformity of temperature (51, 58), start-ups and shut-downs (52), and optimum values of 1,000°C. (26, 37), 1200°C. (4), and 1320°C. being mentioned. If the SO₂ content of the gas is kept at a high value, the tendency of SO₂ formation is reduced (12).

There are 11 references (10, 12, 40, 41, 51, 52, 75, 81, 87, and 89) having to do with the effect of catalysts on the formation of SO₂. Selenium is mentioned (10, 40, 51, 89) as having a positive effect on SO₂ formation, refractory lined burners will produce less SO₂ than a conventional type of iron burner (12, 52), and ferric oxide (41, 46, 75), mild steel (81), aluminum (81) are also mentioned as having catalytic effects.

There are 11 references (1, 2, 10, 15, 25, 26, 35, 37, 52, 55, and 58) having to do with the effect of cooling rates of the burner gas on SO₂ formation. It is mentioned that rapid cooling to 200°C., or below (1, 10, 52, and 55), and a short length of gas travel to the cooler (15 and 55)
are conducive to minimize SO$_3$ formation.

The survey reveals 5 references (33, 43, 48, 52, and 90) wherein it is mentioned that electrostatic precipitators are useful in removing SO$_3$ content from burner gas.

Concerning the presence of SO$_3$ in burner gas, it is obvious sulphuric acid will form when the temperature of the gas falls below the acid dew point and the condensate will then be quite corrosive to a number of alloys, including the stainless steels. It appears that some corrosion problems could be substantially alleviated by the proper operation of sulphur burners and the handling of the resultant gas.

SO$_3$ in Acid Making

There are 8 references (23, 36, 44, 49, 58, 62, 73, and 84) concerning the operation of acid-making systems and the formation of SO$_3$. One reference (36) reports the tower acid system will produce less gypsum than the milk of lime system, and another reference (44) indicates sulphate formation is caused by oxygen in the system and is confirmed by the fact that most of the gypsum is found at the top of the tower. The use of tower exhaust gas as a substitute for air for dilution is reported (49) to have reduced the amount of sulphate formation. It is reported (73) that even when burner gas is low in SO$_3$ some sulphate is usually found in the liquor because of oxidation of the bisulphite by air. While it is possible for the SO$_3$ present in the burner gas to be removed either in the spray coolers or in the acid-making system, it is probably not wise to depend upon this mechanism to reduce corrosion since sulphur efficiency will also decrease.
There were 4 references (44, 51, 68, and 86) having to do with catalytic effects on SO₃ formation in acid-making systems. One reference (44) reports that sulphate formation from bisulphite is not due to the catalytic effect of arsenic as arsine oxide. Selenium (51) is reported to have no catalytic effect in acid making but it does have a positive effect in the sulphur burner. On the other hand, another reference (68) reports that sulphurous acid may be converted to sulphuric by the positive catalytic effect of selenium. Metallic copper is reported (86) to exert a positive effect on the formation of calcium sulphate during acid making, whereas stainless steel has no effect. Further, it was shown that a positive catalytic effect was exerted by the cupric ion, in the absence of copper.

SO₃ in Digesters

There are 5 references (18, 29, 56, 72, and 82) having to do with the formation of SO₃ in the digester. One reference (29) reports that the formation of sulphuric acid takes place in the early stages of the cook and is due to the air in the digester and in the wood. Two references (56 and 82) report methods wherein the oxidizing effect can be minimized by operational procedures such as pre-evacuation of the chips or a pressure manipulation mechanism. A reference (72) indicates that in immobile solutions there is a steady decrease of SO₃ content from the surface to the interior of the solution in the air oxidation of bisulphite liquors. While this may be true for immobile liquors, it appears this effect would not exist within a digester.

Catalysts were mentioned in 6 references (2, 3, 22, 30, 40, and 60) and one (2) reports that sulphate formation in sulphite pulping is
inhibited by carrying out the pulping either in the presence of copper in a discrete form with a large exposed surface, or by circulating the liquor through copper (compare with reference 86). Colloidal sulphur is reported (3) to have a catalytic effect on sulphate formation in digesters. Selenium, colloidal selenium, or selenious acid is reported (30) to have a positive effect on sulphate formation in digesters. Another reference (40) deals with selenium and it is reported that an analysis of sulphite acids prepared from SO₂ derived from Se-containing pyrites indicates that some Se finds its way into the cooking acid no matter how carefully the SO₂ burner gas is washed. Thiosulphate in cooking liquor is reported (60) to have a positive effect upon sulphate formation in digesters.

There were 8 references (20, 53, 54, 57, 66, 67, 80, and 82) having to do with digester or cooking operations on SO₃ formation. Some of these indicate a diversity of findings and some indicate a similarity of findings. Suffice it to say that digester or cooking operations should be reviewed to ascertain the presence of procedures leading to SO₃ formation.

It is worthy of note that one reference (18) reported that the adverse effect of SO₃ in digesters is greatly exaggerated and is not harmful.

Sulphate Formation

There are 9 references (3, 17, 23, 32, 49, 50, 71, 76, and 84) citing a miscellany of mechanisms and reasons for sulphate formation. These are suggested for review as they are expected to provide helpful information in some instances.
There are 5 references (21, 34, 38, 45, and 79) having to do with SO₃ formation and its corrosive effect. Three references (21, 38, and 79) report results on the corrosion of carbon steel by condensed films of sulphuric acid, and the effect of dew point on corrosion. Metal corrosion is reviewed (34) and examples are given of a number of types, illustrated with photomicrographs. Mention is made of the destruction of the protective oxide film on stainless steel by hot gases containing sulphur oxides. A detailed description (45) is presented on materials of construction for sulphuric acid plants.

This relatively small number of references to corrosion indicates several possibilities:

a. Corrosion problems are not serious;

b. Corrosion problems may be serious but have not been recognized as such, or

c. A study is needed to evaluate the problem.

Of these three possibilities the last one is probably the most reasonable. If it became apparent by investigation that corrosion problems do exist, the acid-pulping industry will probably take the necessary steps to alleviate the situation.

In conclusion, a number of the references in the bibliography have been cited specifically with respect to SO₃ formation and its possible corrosive effect on stainless steels. In acid-pulping systems, the calcium base is most vulnerable. However, it has been indicated that soluble-base systems are not immune to corrosion problems. The acidic liquors and the corrosion-resisting characteristics of the stainless steels can be made much more compatible if SO₃ formation is minimized.
ABSTRACTS FROM THE LITERATURE


A mathematical exposition of sulphur burning with accompanying diagrams and charts. Partially insulated burners are unsatisfactory from an operational and economical point of view, as the most favorable conditions are obtained at 800°C. at which temperature the sulphur loss as SO₃ amounts to 8.5%. The higher the combustion temperature of the combustion gases and the less the heat loss, the more efficient will be the production of SO₃. After a high combustion temperature, a rapid cooling to 200°C. should follow to inhibit as much as possible the reaction 2SO₂ + O₂ → 2SO₃. This can be accomplished by water showers and the heated water leaving the showers should be close to 100°C. where the SO₂ content of water is negligible at atmospheric pressure.


Sulphate formation in sulphite pulping is inhibited by carrying out the pulping either in the presence of Cu in a discrete form with a large exposed surface or by circulating the liquor through Cu. Spruce wood chips (1 part), 0.005 part Cu filings, and 4.5 parts sulphite liquor, containing 5% total SO₃ and 1.3% combined SO₃ as MgSO₃, were cooked in a stainless steel digester. The temperature was raised to 110°C, kept there for three hours, raised again in one-half hour to 150°C, and kept there for two hours 40 minutes. The waste liquor contained 0.06% sulphate as compared with 0.13% on cooking.
Studies of sulphate formation made in a sulphite mill operating on calcium-base liquors made from kraft sludge show that the resulting sulphur loss may be of the order of 44 lb. per ton of bleached pulp. The majority of the sulphate formation occurs during the cooking process, and the catalytic effect of colloidal sulphur is believed to be responsible for about 40% of this formation. Serious scale deposition in the digester circulation lines was eliminated by a change from steam injection devices to bottom steaming. Conversion to sodium-base acid reduced sulphate formation by about 68%.


A description, with drawings, of the Texas Gulf sulphur burner and its operation. Owing to the high temperature of combustion (1200°C.) and the high conversion of sulphur to SO₂, negligible amounts of SO₃ are formed.


In acid making, the flue gas from the recovery furnace is passed through towers to absorb the SO₂, the concentration of the SO₂ in the flue gas being in the order of 1%. Large amounts of sulphate were found being formed, but were controlled by heating the absorbing liquor and keeping the oxygen content of the flue gas to a minimum. The spent
liquor was neutralized before evaporation to reduce sulphur losses.


   This contains essentially the same information as the previous article (5).


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   Improvements and developments in the calcium bisulphite process are discussed under the following headings: sulphur melters, tubular melter, sulphur vaporizer (rotary and spray type), combustion chambers, burner gas, coolers (indirect coolers), spray cooler, limestone handling, temperature control, refrigeration, steam-jet refrigeration, recovery plant, chemical bases, and quality control of acid making.


   A description of the Lurgi tower for washing and cooling SO₂ gas by means of which SO₃ formation is reduced to 1.07% of the sulphur used.

Knietsch (Ber. 1901:4083) has clearly established the process of formation of \( \text{SO}_3 \) from \( \text{SO}_2 \). It is known that to avoid the promotion of the formation of \( \text{SO}_3 \), the combustion of sulphur must be so conducted that the temperature of the gases in the oven and in the combustion chamber be either under \( 200^\circ \text{C} \) or over \( 1,000^\circ \text{C} \). Great excess of air and the presence of selenium contribute also to \( \text{SO}_3 \) formation. The gases must be cooled below \( 200^\circ \text{C} \) immediately after leaving the combustion chamber, and this must be done rapidly, so that the gases are not for too long a time in the dangerous temperature range.


The author confines his remarks to the operation of the rotary type of sulphur burner and discusses how sulphur losses in the acid plant may be materially reduced by improving the combustion through the installation of a spray-type burner or the efficiency of the combustion chamber by alterations which will insure a thorough mixing of the gases.


\( \text{SO}_3 \) in burner gases may be formed by the decomposition of sulphuric acid present in the sulphur by atmospheric oxidation. This
amount however is small. In a typical analysis 0.05% sulphuric acid was found in sulphur, this being equivalent to 0.016% of sulphur. A satisfactory method for determining small amounts of $SO_2$ in the gas mixture is given.

In a comparison of the spray-type burner of the Texas Gulf Sulphur Co. with other types of commercial burners relative to $SO_2$ formation, the following conclusions are made. (1) Irrespective of the burner, an increase in $SO_2$ content of the burner gases leads to decreased $SO_2$ formation. (2) The high temperature of 2,400°F. and the high concentration of $SO_2$ prevailing in the spray-type sulphur burner limit the maximum amount of $SO_2$ that can be formed to a value lower than that found in conventional burners. (3) A burner lined with refractory brick will produce burner gases of lower $SO_2$ content than the conventional type of iron burner. (4) No marked advantage is obtained by replacing ordinary steel by special alloy steels, such as KA-2, from the standpoint of $SO_2$ formation. (5) With the conventional type of burner, the temperature range (650-850°C.) at which maximum $SO_2$ formation takes place in the presence of iron is met while the burner proceeds to maximum production and while it is being burnt down. This accounts for surges of $SO_2$ found in the "cooking liquor at various times. 13 references are given.


[In Norwegian]

Recent developments are reviewed, including the Nichols-Freeman furnace, the Trail furnace, the FluoSolids process, and the BASF (Badische Anilin & Soda-Fabrik) furnace, and data are given on their
Factors affecting the formation of supersaturated solutions of CaSO₄ in the neutralization of H₂SO₄ hydrolyzates (I) are: temp., the rate of growth of crystal nuclei, the amount of precipitated CaSO₄, the intensity of agitation, and the presence of colloidal organics. At 75-80°C CaSO₄·2H₂O is formed predominantly; higher temp. leads to the formation of CaSO₄·1/2H₂O which, on cooling to 28-30°C, gives supersaturated soln. The beneficial effect on the prevention of CaSO₄ deposits on fermentation equipment, experienced in filtering partially neutralized solns. through sawdust, has motivated the study of the influence of cellulose sugars (II) on CaSO₄ solns. Boiling the soln. (pH 4.1-4.2), taken from a sedimentation tank, with sawdust showed that these solns. contained more sol. CaSO₄ than untreated. In another expt., sawdust was treated with 72% H₂SO₄, the amount of fermentable sugars detd., and the substrate added to I. The amount of sol. CaSO₄ in I was almost twice as high as in the soln. without II. Neutralizing I with a mixt. of CaO and MgO led to a higher content of sulphate in the soln. as a result of the higher solubility of MgSO₄.

short length of gas travel result in quick cooling of the SO, thus keeping the formation of SO, to a minimum.


In the combustion of sulphur, if the excess oxygen be fixed at 2%, SO, is formed at various temperatures as follows: at 1,100°F., 20% of total sulphur; at 1,500°F., 8.0%; at 2,000°F., 1.0%; at 2,500°F., 0.3%.


The results of translation from pilot-plant studies to commercial operation are described. Because of scale formation satisfactory operation is obtained for 20 hours only. Scale is then removed by operation of the evaporator from regular feed rate of 65 to 180 g.p.m. of recovered distillate, this occupying 4 hours between shut-down and start-up. The net evaporation is 14.8 lb. H2O/lb. steam.


The adverse effect of SO, in the digesters has been greatly exaggerated. Most recent investigations show that SO, is not harmful and some mill operators claim an advantage in having a considerable quantity of SO, in the digesters. 18 references are given.

An improved design for sulphur burners has been developed. The developmental work is described through four stages from the pilot-plant scale to a commercial installation with a capacity of 16 tons of sulphur/day. Using conditions of high mass velocity and high turbulence to accomplish rapid mixing of sulphur and air, it has been demonstrated that the burning can be accomplished in small-volume burners of simple tubular-type construction, using a pulverized, atomized, or vaporized type of sulphur feed. The pulverized type of feed was employed on the pilot-plant scale but has not been demonstrated in a commercial installation. Quality of the burner gas is considered to be as good as from other burners. About 19% by volume of sulphur dioxide could be produced before carry-over of unburned sulphur was observed. Indirect methods indicate that sulphur trioxide formation for the burner and cooling system amounts to between 1 and 3.6 mole percentage of the sulphur burned. 1 table, 8 figures, and 5 references.


The $SO_2$ content (I) of the black liquors was determined after variations in cooking procedures and chip preparation in bronze, stainless steel, and glass digesters, and data is given to correlate the (I) with rate of lignin sulphonation.

In the corrosion of steel surfaces by condensed films of H₂SO₄, it was found that an increased SO₃ content raises the dew point of the condensed films, corrosion increases with dew point for a given surface temperature of 20-45° below the dew point, little corrosion occurs when the surface is at or above the dew point, and after 60 minutes condensation and corrosion vary linearly.


This very extensive investigation describes reaction mechanisms for, among many others, the oxidation of H₂SO₃ and its salts to H₂SO₄ and its salts as affected by various traces of catalysts, O₂, etc.


If the method of direct heating, by which the steam and acid are mixed outside the digester in a special mixer or hydro-heater, is employed, lime formation can be prevented. In this method, steam is admitted in the center of the acid stream by a cone-shaped valve. The main steam line is wide open to this valve and so the main line pressure is always at the back of this valve. At all steam flows, large or small, there is an excess of steam pressure over the acid pressure so that the valve is kept free of acid, consequently local overheating and lime precipitation are avoided. When steam is added
through any form of nozzle, controlled by a valve further back in the line, lime formation cannot be prevented.


   The gases leaving the waste heat boiler at about 200°C. contain 0.1% SO₂. About 0.5% of the total sulphur used is lost as SO₂.


   A spray cooling system for the burner gas is described, by means of which the SO₂ content of the cooking acid is kept to a maximum of 0.03%. Two towers are used for cooling. In the primary cooler, the burner gases are humidified to practically complete saturation with concurrent water sprayed at a rate of 60 gal. per min. from a Spraco nozzle. The rapid cooling reduces the SO₂ to a minimum. The partially cooled gas is further cooled in a larger chamber with countercurrent water sprayed from a nozzle at the top of the chamber at a flow rate of 100 gal. per min.


   In flash roasting, the temperature of combustion (1,000°C.) maintained in the combustion chamber and the rapid cooling of the gases in the waste heat boiler or by other means prevent the formation of SO₂.

Calcium sulphate forms supersaturated solutions which remain in that condition for long periods. Concentrations as high as five times saturation have been produced and maintained for several minutes without precipitation. Finely divided gypsum has a greater solubility than coarse grains but the fine grain solution is an unstable condition, the grain size increasing through precipitation and re-solution. The most recent data show maximum solubility of calcium sulphate as 0.2097 g. per 100 g. of solution at 40°C.; solubility at 100°C. is 0.1619 g. per 100 g. solution. The solubility of "soluble anhydrite" at 151.2°C. is 0.049 g. per 100 g. of solution. Curves are given showing the solubilities of the various forms of calcium sulphate.


The review deals with publications on the operations in limestone-tower and milk-of-lime systems of the calcium- and magnesium-base sulphite processes covering the period 1920-51; only in exceptional cases have earlier or more recent references been included. No claim to complete coverage is made. The review is presented under the subtitles: raw materials (sulphur dioxide, lime and limestone, and water); the preparation of the raw acid, including construction materials; the preparation of the cooking acid; and control and instrumentation. A list of source material is appended.

The formation of sulphuric acid takes place in the early stages of the cook and is due to the air in the digester and in the wood. Increase of the SO$_2$ content of the cooking liquor results in an increase in formation of sulphuric acid. About 20% of the SO$_2$ produced is taken up in the formation of sulphuric acid.


Considering cooking acid from pure chemicals and cooking acid containing selenium, the formation of sulphuric acid decreases with increasing base content. When selenium, in the amount of 0.5 mg./liter and as selenious acid H$_2$SeO$_3$, is added to the liquor, formation of sulphuric acid is more rapid at low base content (below 1%) than at high base content (above 1%); beyond 13 hours' cooking at maximum temperature of 135°C, the formation of sulphuric acid, with increased time, increases continuously above its formation in cooking liquor without selenium. When selenium is added in the form of colloidal selenium, rather than of selenious acid, formation of sulphuric acid is greater.
Following a brief description of the Dorrco FluoSolids system of roasting ores under closely controlled conditions, the plant installations and operating experience of the Brown Company at Berlin, N. H. in roasting pyrrhotite to produce 12-14% sulphur dioxide gas are discussed. Since it was the first unit of its kind—operation started in May, 1952—problems have been encountered and certain changes made. The maintenance of the system has been greater than anticipated; the original construction materials did not withstand the severe roasting conditions and had to be replaced with abrasion- and corrosion-resistant materials in many instances. Nozzles of improved design in the reactor constriction plate had to be installed. Despite repairs, the plant ran 80% of the time during the first year of operation; over 27,000 tons of pyrrhotite were processed, which is equivalent to over 9,700 tons of sulphur. A primary feature of the FluoSolids system is the ease with which the unit can be started up, operated, and shut down.


Scale formation in the evaporation of calcium sulphate solutions was examined in a specially designed evaporator made of glass. The evaporator is described with drawings. Solutions of calcium sulphate were made by dissolving 2 g. desiccated calcium sulphate in 1 liter.
water at room temperature, shaking every five minutes for a half hour and filtering. The evaporation rate with water alone was considered as 100%, and the evaporation rate of calcium sulphate solution as a percentage of the water evaporation rate.

The evaporator was started on water, and calcium sulphate solution added to maintain a constant level in the evaporator, when steam temperature and pressure are kept constant. When 1,000 cc. calcium sulphate solution were added, scale formation was observed after 60 minutes running time. A sharp drop in evaporation occurs at this point, when the rate was 96%, and in the next 60 minutes it dropped off to 50%, from which point it dropped slowly to 20% after 4 hours' total evaporation.

Efficient descalers of the scale formed were found to be: (1) Starch, when added to the solution in amounts of 100 p.p.m.; the nonadherent scale could be removed by finger pressure. (2) Candelilla wax coating, with or without tetraphosphoglucosate, gave a nonadherent scale similar to starch. (3) Resin coating also gave a nonadherent scale easily removed, but the Bakelite varnish coating cut down the evaporation rate to one half the normal rate.


The use of electrofilters to purify the gases formed in the roasting of pyrites is described. By their use the SO₃ content of the acid liquor can be reduced from 0.12 to 0.03-0.06%. Among advantages claimed are minimum formation of calcium sulphate and lessened damage to the equipment thereby.


Metal corrosion is reviewed and examples are given of a number
of types, illustrated with photomicrographs. The protective oxide
film on stainless steel is destroyed by hot gases containing sulphur
oxides.

35. Inderdohnen, J. F., "Recent developments in sulphite pulping;"

Paper Trade J. 126, No. 11:59-60 (March 11, 1948).

The spray cooler permits higher entering gas temperature and
sudden cooling below the critical point to keep SO₃ formation to a
minimum. Any SO₂ present is washed out to maximum residuals of 0.03
to 0.04% of sulphur used; sublimed sulphur is also washed out.

36. Jensson, G. D., "Limestone or burnt lime for sulphite mills;" Paper

20, No. 14:12 (1917).

A critical comparison of the two systems of making sulphite
cooking acid is given. J. considers the tower system easier to
operate, gives a stronger acid with less CaSO₄ formation, requires
less power to operate, and is easier to maintain than the milk of
lime system.


In flash roasting, the particle roasts at a temperature in ex-
cess of the surrounding gas temperature. Under conditions where the
particle temperature is in excess of 1,000°C. and the gas temperature
less than 1,000°C., the atmosphere of SO₃ immediately surrounding the pyrite particle will approach the particle temperature and the formation of SO₃ cannot take place. By limiting the partial pressure of oxygen adjacent to the particle, narrow limits between the particle and gas temperatures at about 1,000°C. can be maintained and so the combustion chamber can be made practically free of SO₃. The low oxygen content of the gas and its rapid cooling during the SO₃ formation range permit only the smallest quantity of SO₃ in the gas from the waste heat boiler; the further rapid cooling in the scrubbing towers results in the admission of the minimum quantity of SO₃ to the limestone absorbing towers. At the St. Lawrence mill, there is never any trouble with calcium sulphate either in the limestone towers or subsequently in the acid system.


Studies of the corrosion of cooled steel probes by flue gases contg. SO₂ and SO₃ show that for tests up to 24 hr., there is a reduction in corrosion rate after 8 hr.. In the presence of corrosion products, the corrosion continues even when the metal temp. is raised to or above the acid dew-point temp.


Among the advantages of a hot acid system is cited the almost total absence of lime in fittings exposed to direct action of steam.

A qual. test for Se in Ca bisulphite liquor consists of b. the soln. with HCl, when the characteristic red color of Se appears. Conc. solns. are necessary when the amt. of Se present is small. For quant. detn., 3 to 5 l. of cooking liquor are conc. to one l., made distinctly acid with HCl and b. to expell all SO₃. A little ZnCl₂ is added, b. continued for some min. and the soln. allowed to stand 24 to 48 hrs. in a warm place. The Se ppts. and the soln. is filtered through a dense asbestos mat into a combustion tube and the Se detd. according to the author's method previously described (Z. Angew. Chem. 25:514-18; Papier-Ztg. 37:374-6, 411-12).

Analysis of sulphite acids prepared from SO₂ derived from Se-containing pyrites shows that, however carefully the SO₂ is washed, some Se finds its way into the cooking acid where its presence is extremely undesirable. (Ed. note: Se catalyzes reaction SO₂ + O = SO₃.)


The catalytic effect of ferric oxide (present in the roasted ore) in the formation of sulphur trioxide at various temperatures is discussed at length. Ferriferous oxide appears to be an intermediate product. The author has amplified the data of Remmler, Krull, and Kuhn (cf. Herstellung der Sulfitlauge, Berlin, 1925) by determining the volume percentage of sulphur trioxide formed in sulphur dioxide in the range of 371-550°C, for which full analytical data are given. A graph prepared by Schwarz-Bergkampf is included which can be used
in determining the catalytic effects of platinum vanadium pentoxide, quartz, ferric oxide, etc. on the formation of sulphur trioxide at various temperatures. In a furnace at the sulphite mill Maxau, catalytic effects were especially marked between 570 and 600°C. In conclusion, a brief reference is made to the new fluidized-bed furnace without hearths developed by the Badische Anilin- und Soda-Fabrik and built by Lurgi-Chemie with considerably reduced sulphur trioxide formation.


The SO₂ content of the gases with this burner is 19.5 to 20.3% as compared with a theoretical maximum of 21%. The nearer the SO₂ content of the gases is to 21% the less SO₃ is formed. With the high gas concentration and the ceramic lining and elevated temperatures of this burner, the SO₃ content of the gas going to the coolers is 0.14% of the sulphur burned in comparison with 1.45% in conventional burners. With the lowered SO₃ in the finished gas, the calcium sulphate in the cooking liquor is proportionately reduced.


When SO₂ gas is obtained by the roasting of pyrites, it can be purified by the Cottrell process in two stages—the first at 1,000-1,200°F. in a special precipitator of brick and steel to remove dust, and the second for the removal of SO₃ mist from the cooled gases.
The second stage is sufficient when the $SO_3$ gas is obtained by the burning of sulphur.


The formation of gypsum in a tower acid prepared from pure $SO_3$ gas is not due to an equilibrium between sulphite and sulphate ions, for pure bisulphite liquors can be prepared free of sulphate; nor is it due to the catalytic action of arsenic as arsenious oxide. The oxidation of sulphite to sulphate is due to the partial pressure of oxygen and this is confirmed by the observation that most of the gypsum is found at the top of the tower.


Sweden's annual consumption of $H_2SO_4$ since 1939 has been 50 kg. per capita as compared with 100 kg. in the U. S. Construction materials of a typical Swedish pyrites contact plant follow this order: For the pyrites drier located above the furnace Fe has been largely superseded by "Sicto-material" (86% SiC) to resist corrosion by the moisture of the ore. The air-cooled raking arms of the Herreshoff exposed to temperatures of 500 to 900$^\circ$ are of flame-hardened steel with 13% Cr. The vertical Fe shaft is protected with masonry. Old-time cast-iron ducts from the burner often develop cracks from heat stresses in which localized corrosion took place. Later practice employs mild steel, no less vulnerable, perhaps, but more easily repaired. Ducts of 12-13 mm. thickness should last 15 years.
Stainless steel is too costly for the purpose. In some plants, ducts are lined with brick, but in such cases temperatures in the dust filters may rise high enough (550°F) to cause buckling of the plates. Gas washers are of Pb lined with brick to protect the metal from temperatures of 450 to 500°F. The tower top is water-cooled to 80 to 90°F. Towers are steel-banded to give them structural stability. The 66% wash acid leaving the tower at 70-80°F goes to a reservoir containing Pb cooling coils. Pumps and valves of hard Pb (7-10% Sb) are vulnerable to mechanical abrasion by the sludgy acid. High Si Fe, resistant to H₂SO₄, would serve well, but unfortunately it is sensitive to the dissolved SO₂. Construction of the As tower in which Pb, Se, Te, As, and SO₃ are removed is similar to that of the washer. In the drying towers that follow H₂O is reduced with a concentrated H₂SO₄ wash from 10-15 to 0.5 g./cu. m. Construction is of acidproof masonry; packing, Raschig rings. The compressor housing is of cast iron; the rotor of mild steel. If the temperature is below 40-50°F the highly gas-impervious polyvinyl chloride can be used for gas ducts. The C-steel tubes of the converter are exposed in certain sections to scaling temperatures so that their life is limited to about 5 years. In the heat exchangers the critical requirement is low H₂O content since temperatures may go below the dew point in some places; drying below 1 g./cu. m. is mandatory. A 5% Si cast iron may serve for gas and acid values. For pure SO₃, an 18-8 steel with 2% Mo has been used successfully. Finished 98.5% acid even at temperatures of 60-70°F is stored in Fe tanks. Diluted to 95-96% with 78% acid, temperatures should be kept below 30-35°F to reduce possibility of corrosion. Physical and chemical properties of numerous construction materials are summarized.
Pure sulphur dioxide free of oxygen and sulphur contaminants can be continuously prepared by burning sulphur, hydrogen sulphide, or sulphur-containing ores and passing the gases through a purification zone containing a mixture of iron oxides (50% of Fe$_2$O$_3$ and 50% Fe$_3$O$_4$). The combustion should be carried out with a controlled quantity of air, depending on the state of oxidation of the material being burned. A flowsheet of the operation is given.

The object of this invention is the provision of a method for producing from sulphide ores, particularly pyrites, sulphur dioxide substantially free from sulphur trioxide, free oxygen, and elemental sulphur, and to leave the metal sulphide substantially free of sulphur. Sulphide ore in a finely divided state is suspended in an oxidizing atmosphere of controlled temperature so that sulphur is liberated with the formation of a minimum amount of metal oxide. The liberated sulphur is removed from the fluidizing zone and then burned under controlled conditions to produce sulphur dioxide with a minimum amount of sulphur trioxide. The metallic ore, in a fluidized state, is then converted to the oxide by treatment with hot oxidizing gas.
The author gives preliminary data on the experience gained in the roasting of pyrites in the Kuusankoski sulphite mill of Kymmene Aktiebolaget. For a period of six months the mill has roasted Finnish flotation pyrites in a fluidized-bed furnace of the Badische Anilin- and Soda-Fabrik, constructed by Lurgi-Chemi. As soon as the feeding apparatus had been partially reconstructed, the roasting was successful. The guaranteed capacity of the furnace is 80 tons of pyrites per day; the mill has not yet reached full production, so that the furnace has so far operated with a load of 50-60 tons. However, there seems to be no doubt that not only can the full load be carried, but also that the maximum capacity lies considerably higher. The furnace gases contain about 14% of sulphur dioxide and, after passing through the washing tower, 12-13%. The sulphur loss in the ash is about 1.5%.

Heat in the form of steam is extracted from the gases to the extent of about 1.2 kg. of steam/kg. of pyrites. The La Mont boiler is constructed for a pressure of 40 atm. and a capacity of 4.2 tons of steam/hour. For the purification of the gases both cyclones and electrical devices are employed; two washing towers are installed between the dry and wet electrical purification stages. After passing the purification installations, the gases are completely free from ash and other impurities.
The reclamation of sulphur dioxide produced as waste from several industries has received a great deal of attention and research. In 1947, the Abitibi Power and Paper Co. operated the acid plant of its mill at Fort William on liquid sulphur dioxide manufactured by the Canadian Industries Ltd. at Sudbury, Ont., where it was obtained from the waste gases from the International Nickel Co. smelters. The experiments were successful, but the cost was still too high compared with native sulphur, and after a fair trial the operations were discontinued. In 1951, when sulphur allocations came into effect, equipment to use liquid sulphur dioxide was installed at the Abitibi mills at Smooth Rock Falls, Iroquois Falls, Sault Ste. Marie, and Sturgeon Falls. The author describes the equipment and operation of the acid plant on liquid sulphur dioxide at the Smooth Rock Falls mill, where it has been in operation since January, 1953. The main items of equipment are: storage tanks, compressors, heat exchanger, flowrater for metering the liquid sulphur dioxide being used, and evaporators to vaporize the liquid into gas for use in the Jenssen towers after dilution. Prior to the start-up, a thorough training period was conducted to familiarize all personnel concerned with the use of the new equipment. In operation, the liquid sulphur dioxide system is much easier to handle than the sulphur-burning system. Start-up or shut-down can be performed in a matter of five minutes, whereas with sulphur burning, these operations would take four to five hours. Equipment maintenance is low, and the extreme flexibility of the
system allows repairs and cleaning during the week. The loss of a considerable volume of warm water from the Jenssen coolers has necessitated the heating of the water for acid making by steam, and the formation of sulphates was troublesome until tower-exhaust gas was used in place of air for dilution.


App. is described by which the direction of flow of liquor in the preheater of the circulation system is reversed from time to time to prevent accumulation of CaSO₄ scale in the preheater.


By proper regulation of the air supply and by insulation of the combustion chamber, it became possible to produce a gas of 15-16% SO₂ with a decrease of the SO₃ content. If the greater part of the air for combustion was introduced as secondary air, there was no appreciable effect on SO₃ formation. When excess air comes in contact with the acid, oxidation is effected in the acid tower. A noticeable decrease in the SO₃ content of the cooking acid is obtained when the circulation in the acid tower is reduced. Selenium does not act as a catalyst for SO₃ formation in the acid tower, though it does in the sulphur burner. SO₃ formation can be reduced 60% by control of the combustion and of the temperature in the combustion chamber and, in addition, by reduction of the circulation in the acid tower.

Under continuous operation of the conventional type unlined rotary sulphur burner, a conversion of 1-2% of sulphur to $SO_2$ is to be expected, while a burner lined with refractory brick will produce burner gas of lower $SO_2$ content.

$SO_3$ formation will be at a maximum while the burner is being started or burned down, due to the exposure of iron and its catalytic effect on $SO_3$ formation at a certain temperature range. Through cooling of the gases below 46°C., the boiling point of $SO_3$, the latter is condensed to a fine mist difficult to dissolve. The wet Cottrell method so far gives most satisfaction in the elimination of $SO_3$ from the burner gases.


The cooking liquor was prepared from a commercial hydrated lime, containing 98% calcium hydrate, and liquid $SO_2$. From the results obtained, it would appear that (1) any appreciable quantities of sulphate are found only at the end of the cook; (2) the formation of sulphates is not governed by the temperature; (3) a free $SO_3$ content of over 1% at the end of the cook seems to indicate a low sulphate content compared with a free $SO_2$ content of under 1%, the sulphate content showing a range of 0.10-0.24% considered as percentage of $SO_2$ in the liquor.

A discussion of the roles of \( \text{SO}_3 \) and \( \text{CaO} \), and their proper concentrations, in the mechanism of delignification during a sulphite cook. The action of \( \text{CaSO}_4 \), during a sulphite cook, and how to minimize its harmful action, is also discussed.


To minimize the formation of \( \text{SO}_3 \), the gas must be transferred to the washing tower through as short a distance as possible and should be cooled as quickly as possible. Construction of ovens and towers is described. Analysis of a sample gave: total S acidity 3.20, combined \( \text{SO}_2 \) 1.09, free \( \text{SO}_2 \) 2.11, \( \text{CaO} \) 0.94, \( \text{SO}_3 \) 0.03, \( \text{CaSO}_4 \) 0.06%.

The gases enter the tower at about 500° and go out at about 80°. The wash water at about 70° circulates at the rate of about 800 l. per min. The \( \text{SO}_3 \) content never rises above 0.03%.


After pre-evacuation of the chips, the amount of sulphuric acid, which can be formed by the oxidizing effect of residual atmospheric oxygen in them, is very small compared with that formed by the oxygen of the water in the preparation of cooking liquor, and other atmospheric oxidation.

The per cent reducible S and the SO₃ and lignin held in unbleached pulps are correlated with and controlled by the temp. rise in the digestion. Above certain limits the above components are detrimental to brightness. These limits are discussed together with the time of penetration of the acid into the chips prior to the attainment of the crit. temp. (110°), and the purity of the H₂O. A slow uniform cooking temp. led to unbleached pulps of satisfactory brightness (i.e., 61).


Author describes operation of a sulphur spray burner with a spray-type cooling tower in conjunction with a Jenssen cooler. By this equipment the raw acid had an average content of 0.02% SO₃ with a minimum value of 0.015%, whilst with the old system consisting of rotary burners, combustion chamber and Jenssen cooling system, the SO₃ content of the raw acid averaged 0.055% with a minimum value of 0.049%. The decrease in SO₃ content by the new system is attributed to (1) reduction in moisture content of the sulphur as fed to the burner, (2) more uniform maximum burner temperature and (3) absorption of SO₃ by the water in the spray cooler. The result of the decrease in SO₃ content of the raw acid is the almost complete elimination of lime formation in the digesters, since the lime contains 6% calcium sulphate and can be easily detached by shaking the digester; with the old system the lime contained 15% calcium sulphate, was very hard and required time and labor for its removal.

The author proposes some corrections in the mathematical formulae of Sylwan (78).


Spruce (Picea jezoensis) was treated with sulphite cooking liquor to which no thiosulphate (I) was added; sulphate formation was very small, not exceeding 1 g./l. at the end of the cooking period. When I was added, the sulphate exceeded 1 g./l. and, within a few hr., the liquor was satd. with CaSO₄. When more than 2 g. S₂O₃/1. was present sulphate increases occurred after 7 hr., and appreciable amts. of the free lignosulphonic acid were probably present in chips. The pulp formed then contained much more condensed lignin and had a brownish black color. The I content (2g. S₂O₃/1.) in the cooking liquor interfered with the cook, irrespective of the Ca-base content in the liquor. There are many substances which produce I by interaction with the cooking liquor, such as sugars, S, and HCOOH, but their detrimental effects upon cooking liquors are probably smaller than is that of I initially present. The sulphate-formation curve can be taken as an index of the overall decompn. effect of these substances. The SO₄ content can be used as an index in detg. cooking conditions in the production of rayon pulp as well as the color of the product.
The decomposition of sulphite cooking liquor proceeds faster the higher the cooking temperature. It is further catalyzed by the presence of sugars, thiosulphate, formic acid, and other compounds which find their way into the acid tank with recovered cooking liquor and relief gases. Between charging operations in batchwise digestion, commercial cooking liquor is held in the tank for some time at 50-90°C. The effect of prolonging the storage beyond the customary time limits on the decomposition of the cooking liquor was investigated, using sulphate formation and pulp quality (viscosity and lignin content) as criteria of liquor deterioration. Spent cooking liquor, blown from the autoclave at an early stage, was treated for 4 hr. at 70°C to serve as control. One part of this early blow liquor, or 1 part (by volume) of the final spent liquor, was mixed with 3 parts of fresh cooking acid for two parallel cooking experiments. The mixture containing the early blow liquor showed negligible decomposition when treated for 4-8 hr. at 100-115°C; slight degradation occurred after 12 hr. and relatively more deterioration after 24 hr. For the mixture containing the final spent liquor, sulphate formation and residual lignin were somewhat higher than in the control run after 4-8 hr. at 100°C, with insignificant further changes up to 24 hr. The results indicate that the use of fully spent liquor in proper admixture with fresh liquor will cause no trouble in sulphite pulping. 5 tables, 8 figures, and 9 references.

A sketch is shown of a simple app. for removing S and SO₂ from burner gas, based upon filtering the gases through a layer of sawdust from 18 in. to 24 in. thick.


Recent improvements to the acid plant and relief-recovery system of the Crown Zellerbach mill at West Linn, Ore. are described. To obtain better combustion control the three small sulphur burners were replaced with large single units; to hold the raw acid strength up during the hot summer months, a raw acid booster tower and gas compressor were installed. Three new units (a pressure tower, atmospheric tower, and tail-gas tower with necessary piping, pumps, and valves) were added to the hot acid accumulator of the relief-recovery system. This installation greatly improved the digester circulating systems which previously had given considerable trouble because of scaling and corrosion. Cooking-acid strength has now been sufficiently raised to permit the installation of chip packing with steam; this resulted in an increase of 7-8% in digester production.


In a system for evap. spent sulphite liquors part of the circulating liquor is drawn off and introduced into another circulating system, which consists of a heat exchanger with a circulating pump.
In this system the liquor is kept at such a temp. (e.g. 160-170°) that the incrustant matters (e.g. CaSO₄) are pptd. From the circulating system a quantity of liquor equiv. to the liquid introduced is withdrawn for evapn.


Practical application of the method to the analysis of S burner gases from sulphite pulp mills showed the presence of 0.033 to 0.28% by vol. which represents a loss in S of 0.20 to 1.93%.


A process of producing sulphur trioxide- and sulphur-free sulphur dioxide gas from pyrite is claimed. A fluidized bed of finely divided pyrite particles (I) is established and maintained in a roasting zone and a gas-bearing free oxygen is passed through at fluidizing velocity. (I) reacts with oxygen at roasting temperatures to yield a gas (II) of sulphur and sulphur dioxide. Roasted (I) containing less than 2% by weight of sulphidic sulphur are discharged and oxygen is supplied to (II) to convert free sulphur to sulphur dioxide; over-oxidization to sulphur trioxide is prevented by maintenance of a trace of an entrained iron-bearing compound as a buffer.


The sulphite (Ca & NH₃ base) pulping characteristics of 4 samples
of P. silvestris (I) from the Leningrad area were studied, and detailed results are given. Results are given of a no. of mill trials on Ca-NH₂ base cooking of (I); at a max. temp. above 130⁰, the cook tended to burn; resulting in the formation of S and CaSO₄, a rapid drop in SO₃ concn., low brightness pulp, soft dark screenings, and an exceedingly high dirt-count pulp.


A study of the change of the sulphate content in a liquor during cooking and during blowing of the digester. Tabulated results show that the sulphate content was high at the beginning of the cook while decrease was noted when the temperature increased. The sulphate content decreased during the relief period. During the period of displacement with water while the liquor was being drained, the sulphate content increased as the temperature of the waste liquor decreased. From these variations it may be assumed that the formation of sulphate is sufficiently high to cause precipitation of calcium sulphate. The values obtained seem to indicate a supersaturation during the cook, rather than a chemical equilibrium. In cooks of rayon pulp, precipitation occurred during the cook, but there was an increase in the solubility of the calcium sulphate during the last stages of the cook and also dissolution of calcium sulphate during displacement in the drainage period. In can be concluded that the manner of removal of waste liquor plays a large part in the sulphate content; it should be removed at as high a temperature as possible.

Conversion of sulphurous acid to sulphuric acid is catalyzed by presence of selenium.


This depends on the absorption of the gases in NaOH, forming NaHSO₃ and Na₂SO₄. The former reacts with HgCl₂ with the liberation of HCl, which is thus a measure of the SO₂ present. SO₃ may then be found by difference. The use of this method indicates the presence of Ca(HSO₃)₂ in sulphite liquors.


Sulphite waste liquor is neutralized with lime, oxidized with O under high pressure at 230-330°C to CaSO₄ and CaCO₃ which are sepd. and roasted at 1280-1600°C to give CaO and SO₂. The CaO is suspended in water and treated with the SO₃ to give fresh Ca(SO₃H)₂ cooking acid.


Factors affecting the dissolving rate of CaSO₄·2H₂O (I) and CaSO₄ are studied for the purpose of increasing the understanding of the formation of incrustants during the evaporation of Ca-base spent sulphite liquor. Literature and theoretical considerations are reviewed,
and experiments with rotating cylinders of (I) and CaSO₄ in H₂O as well as aqueous solutions of glucose, NaCl, dichloroacetic acid, SO₂, HCl, and HNO₃ are described. The dependence of dissolving on temperature, viscosity, flow rate, ionic strength, and pH are evaluated. The results are discussed relative to optimum conditions for dissolving (I) in evaporating equipment. The highest dissolving rates for (I) and CaSO₄ were with 23% HNO₃ solution.


In the air oxidation of bisulphite liquors, there is a steady decrease of the SO₃ content from the surface to the interior of the solution, and the surface layer diffuses very slowly into the interior layers; this is observed with immobile solutions. Calcium liquors form a protective layer of calcium sulphate on the surface, thus inhibiting oxidation in the inner layers of the liquor. Magnesium liquors are just as stable as calcium liquors, though they do not form a protective layer due to the solubility of magnesium sulphate; the slow diffusion of the sulphate into the interior from the surface, however, causes the stability of the solution, as a whole, to oxidation. In testing the liquor for SO₃ content, the greatest proportion is found on the surface layers and the SO₃ content decreases as the sample is taken at increasing depths.

 Even if the absorption of the gases from the furnace is carried out as completely and carefully as possible, small amounts of gypsum are usually found in the acid due to the oxidation of bisulphite by air.


 The present status of the knowledge of fluidization and present and potential applications are surveyed. The roasting of pyrites to sulphur dioxide and the purification of sulphur dioxide from sulphur trioxide are listed as techniques of interest to the pulp and paper industry; the former is already in commercial operation.


 By the use of a "Chemco" spray sulphur burner and furnace, it is possible to produce a gas containing 18% SO₂; also, by partial recirculation of the SO₂, it has been possible to keep below the critical temperature for the formation of SO₃ by the catalytic action of iron oxide.


 The purer the sulphur the less the chance of introducing catalysts favoring the formation of SO₃ at low enough temperatures. The burners should not be overloaded, otherwise excessive amounts of air are required in the combustion chamber and an excess of air promotes
formation of SO₂; in addition, the coolers are overloaded and the SO₂ formed is not properly removed.

A method of testing the gas issuing from the cold end of the coolers is given and results of some tests are tabulated.

When the gases come in contact with the tower acid, free sulphur and SO₃ are entrained in a degree depending on the speed of the gas; pentathionic acid (H₅S₅O₆) is formed and it reacts with calcium ion to give calcium pentathionate H₅S₅O₆ + Ca⁺⁺ → CaS₅O₆ + 2H⁺; calcium pentathionate then decomposes in part to give calcium sulphate, sulphur dioxide and free sulphur: CaS₅O₆ → CaSO₄ + SO₂ + 3S, this decomposition probably depending on the concentration of the calcium ion. The calcium sulphate formed does not appear to dissolve. Methods are given for determining the calcium sulphate, SO₃ and free sulphur in the raw acid. The proportion of calcium sulphate to free sulphur obtained in the determinations agreed well with the conception that they are formed from calcium pentathionate. Some of the calcium sulphate and free sulphur is deposited in the settling and storage tanks and can be determined in the sludge. 12 references are given.


In a process for treating waste sulphite liquor, the liquor is recycled through zones of heating, vaporization, and desupersatn. A raw liquor having about 5-15% by wt. of total org. and inorg. solids is condensed in a continuous process to a liquor having about 50-65% by wt. total solids by heating the liquor to 215-40°F. and
evap. the water. Ptn. and growth of crystals of inorg. solids, i.e. CaSO₃ and CaSO₄, are enhanced by the addn. of CaSO₄ crystals with the make-up raw liquor. The concd. liquor can be used as a fuel for heating and vaporizing the raw liquor.


Modifications in the methods for determining SO₂ and SO₃ are given in order to calculate the efficiency of the acid tower from the composition of the gas going to the tower and of the gas leaving it.


Lab. app. and techniques are given for sampling and analyzing H₂SO₄ condensing from a hot gas mixt. of known water vapor and SO₃ contents. A change of the H₂SO₄ content of the gas phase from 0.007% to 0.07% by vol. (a variation in the dew point from 160° to 205°) caused no change in the concn. of condensate at a selected temp. The concn. of the condensate is a function only of the surface temp. and the water vapor content of the gases. There is a peak in the rate of condensation at a surface temp. approx. 40-50° below the dew point. The magnitude of this peak increases with increasing dew point. The first stage in the transfer to the surface is the formation at the dew point temp. of mist particles containing H₂SO₄ and water. For surface temps. just below the dew point, only a small quantity of acid will diffuse to the wall under the influence of the slight temp. gradient. Below a crit. surface temp., the particles are of such a
size that there will be a slow rate of diffusion to the surface and hence a low rate of condensation.


A discussion of the chem. control of the sulphite process by a rational control of the liquor used in each digester charge. The condition of the chips as to moisture content and sp. gr. play an important part in the control of the process and curves are drawn illustrating the variations in the quantity and strength of the liquor used, resp., with the moisture content and the sp. gr. of the chips. With increasing moisture content the total vol. of liquor is reduced and the same applies to the strength of the liquor although in a different degree for different sp. grs. The content of CaSO₄ in the liquor is greater in the summer than in the fall of the year, the proportion of the Ca combined as sulphate being 15.1% in the former period as compared to 12.8% in the latter. The proportion of combined to total sulphurous acid is likewise greater in the summer than it is in the autumn. Various tables of exptl. data are presented illustrating the use of Winkler's method for the analysis of sulphite liquor.


The rate of catalytic oxidation of SO₂ on the surface of mild steel aluminum sprayed and aluminized steel is reported. The effect of variation in temperature, gas velocity, and concentration of SO₂ has been measured. The presence of water vapor has been shown to inhibit catalytic oxidation on the surfaces tested. The catalytic activity of mild steel increases considerably upon exposure; aluminum
sprayed specimens exhibit a maximum in catalytic activity after 7-12 hours' exposure with a decrease upon further exposure; aluminized steel specimens show constant catalytic activity. Coating steel with aluminum considerably reduces the rate of catalytic oxidation of sulfur dioxide.


Following a brief introduction on the general purpose and advantages of the so-called Vilamo process, the authors discuss some fundamental factors of the sulphite process, such as the size of the chips, cooking temperature, time for bringing to maximum temperature, and the composition of the cooking liquor. The possibilities of increasing the rate of penetration of the cooking liquor and thus decreasing the time for bringing to temperature are reviewed. A short summary of the Canadian Va-Purge process is given, and the Vilamo method is described briefly. According to this procedure the air is removed from the chips after the liquor has been pumped into the digester by increasing and dropping the pressure; the complete removal of the air depends upon loosening or breaking the pit membrane as a result of the abrupt drop in pressure. Wet wood requires more drops in pressure than dry wood. During mill runs it has been found that the relief gases contain only a fraction of the amount of air present in the relief gases of regular cooks. Among the advantages of the Vilamo method the authors claim: lower wood consumption because of lower cooking
temperature and increased calcium oxide content of the cooking liquor, a decrease in the consumption of sulphur, and elimination of calcium sulphate troubles. The quality of the pulp is uniform, even if the moisture content of the chips varies.


A scheme of analysis is indicated whereby sulphite, sulphate, and thiosulphate may be detd. in the presence of one another and by this means the occurrence of varying amts. of sulphates and thiosulphates in sulphite cooking acid was established. It was further shown that:
(1) blowing air into the cooking acid causes rapid oxidation of the $\text{SO}_2$ to $\text{SO}_3$; (2) on long standing, monosulphites and gypsum sep. out, $\text{SO}_2$ being set free; (3) over-saturation of the sulphite acid with $\text{SO}_2$ causes a loss of strength due to sepn. of monosulphite and gypsum.


The formation of sulphuric acid can be greatly reduced by adding small quantities of sulphite waste liquor to the water used for acid preparation. (Investigation carried out at the Wood Chemistry Dept. of the Swedish Wood Research Institute of the Central Laboratories of the Cellulose Industry.)

The formation of $SO_3$ depends on the temperature of the gas before cooling and on the oxygen content. The furnace should maintain a uniform temperature of about 1,000°C before the cooling of the gases, which should be effected as rapidly as possible. The temperature and the analysis of the gases should be constantly controlled with accurate measuring instruments.


The author describes the application of laboratory techniques to two mill problems in sulphite acid manufacture. In the first, the catalytic effect of copper and stainless steel on the formation of sulphates during the acid-making process was investigated. In the second example, an attempt was made to determine the effect of the particle size of the base on the course of the reaction, specifically on the ratio of combined sulphur dioxide (I) to total sulphur dioxide (II) during the acid formation. The results of the first experiments were quite satisfactory; they indicated that metallic copper exerts a positive catalytic effect on the formation of calcium sulphate during acid making, whereas stainless steel has no effect. Further work confirmed the assumption that the increased sulphate content resulted from the presence of copper and not from some other catalyst accidentally present; it was also shown that a catalytic effect was exerted by the cupric ion, in the absence of metallic copper. In the second series of experiments on particle size, results to date have been less
conclusive because of the difficulty of obtaining reliable tests of (II) and free sulphur dioxide (III) in the early stages of a batch of acid. Some tests indicate, however, that the ratio of (I) to (II) is higher during the early stages of acid formation with fine particles than with coarse; i.e., when fine sludge (100 mesh or finer) is used, there is little build-up of (III) until the (I) has reached a maximum, whereas with coarser sludge (100 mesh or more), the (I) reaches a maximum less quickly, and (II) at the time of maximum (I) is likely to be higher. This indicates that a fine sludge is desirable if a high (I) or high ratio of (I) to (II) is sought. The experiments to date do not indicate that any marked improvement could be secured by an attempt to separate the finer fractions of sludge for use in the acid plant. The effect of such a step on overall mill operation would require some study before any changes could be made.


The gases obtained in the burning of sulphur contain valuable heat energy which can be recovered and put to use. Some experience with the heat recovery equipment (a stationary, spray-type sulphur burner operated in conjunction with a waste-heat boiler) at the mill of the Restigouche Co. at Atholville, N. B., are described. Data are given on heat recovery at various sulphur-burning rates. The installation of the waste-heat boiler permits the recovery of about 80% of the heat of combustion of sulphur. In a working period of 21 months, the SO₃ content of the cooking liquor increased from 0.4 g./l. to 1.1 g./l., probably because of the deposition of an ash containing iron salts on
the tubes of the waste heat boiler. Details are also given on instrumentation, maintenance, effect on the sulphate content of the cooking liquor, and the deleterious effect of the sulphur ash on heat-transfer efficiency.


In the burning of sulphur, below 400°C, SO₂ is formed; from 400-800°C, SO₃ is formed as well as SO₂, from 800-1,200°C, SO₂ is formed and above 1,200°C, SO₃ is formed as well. The burners should therefore be operated around 1,000°C. Author gives a table showing the volume of air required to produce a certain volume % SO₃ in the burner gas. The volume of air admitted to the burners is very important as far as prevention of SO₃ formation is concerned.


All pyrites used for the preparation of sulphite liquor contain some selenium, and its catalytic effect in converting sulphite to sulphate is five hundred times that of free sulphur. 1.4 mg. selenium per liter of liquor causes intense darkening of the liquor, charring of the wood and precipitation of calcium sulphate when treated in an autoclave for 10 hours at 125-130°C, and under pressures of 3-4 atmospheres.
91. Zopf, E., "Electrical gas purification for the pulp industry," Papier-

The electrical purification of $SO_3$ gas by the Cottrell-Moeller
process is described. $SO_3$ formation by this purification is reduced
to a minimum by elimination of iron oxide dust, arsenic and selenium
from the gas.